

## $^{27}\text{Al}$ , $^1\text{H}$ NMR studies of supported $\text{LiAlH}_4$ and $\text{Pd-LiAlH}_4$ as reagents for dechlorination of chlorobenzene

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Received 7 February 1994; accepted 30 March 1995

### Abstract

The reactivities of  $\text{LiAlH}_4$  and  $\text{LiAlH}_4$ -Pd supported on porous carbon 'Sibunit' in dechlorination of chlorobenzene under mild conditions and their  $^1\text{H}$ ,  $^{27}\text{Al}$  high resolution solid state NMR MAS spectra are reported. Supported hydrides demonstrate better reactivity compared with  $\text{LiAlH}_4$  in ether-toluene solution.  $^1\text{H}$ , and  $^{27}\text{Al}$  NMR MAS spectra of supported  $\text{Pd-LiAlH}_4/\text{Sibunit}$  suggest the formation of complex hydrides on the surface.

*Keywords:* Chlorobenzene; Dechlorination; Hydrides; NMR; Palladium

### 1. Introduction

Design of the new processes for the efficient removal of high toxic chlorinated aromatic compounds is attracting much attention [1]. It is known that the reducing properties of  $\text{LiAlH}_4$ ,  $\text{NaBH}_4$  and  $\text{MgH}_2$  increase in the presence of salts or complexes of transition metals [2–4]. In some cases this even allows reduction of chloro- and bromo-benzene which usually cannot be reduced under mild conditions.

A study on the mechanism of transition metal-assisted reduction reaction with  $\text{LiAlH}_4$  has been recently published by Osby et al. [5]. It was shown that in the presence of  $\text{Co(II)}$  chloride,  $\text{LiAlH}_4$  produced cobalt aluminide which catalyzed the reduction of several substrates, alkyl halides among them.

Here we show experimentally that  $\text{LiAlH}_4$  and  $\text{Pd-LiAlH}_4$  supported on porous carbon (Sibunit) can be used for dechlorination of chlorobenzene at 70 and 22°C.  $^{27}\text{Al}$  and  $^1\text{H}$  NMR MAS spectra suggest the formation of complex hydrides in  $\text{Pd-LiAlH}_4/\text{C}$  samples.

### 2. Experimental

#### 2.1. Preparation of samples

Porous carbon material Sibunit produced from gaseous hydrocarbons was described in detail in [6,7]. We used for our experiments Sibunit with the following characteristics: composition (wt.%): carbon –99.4; sulfur –0.03; ash –0.2 and surface area from adsorption of argon –280  $\text{m}^2/\text{g}$ .

Sibunit itself or Sibunit with the surface containing supported Pd particles (hereinafter  $\text{Pd/C}$ )

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were impregnated with ether solution of  $\text{LiAlH}_4$ . Excess solution was removed by evaporation and 3 h. drying at  $20^\circ\text{C}$  in vacuum. The obtained reagent contained 10 wt%  $\text{LiAlH}_4$ . 10% Pd/C catalyst was prepared by impregnation of Sibunit with solution of PdCl in aqueous hydrochloric acid and followed by the reduction [8].

Before impregnation the support (Sibunit) and Pd/C were calcined at  $500^\circ\text{C}$  in vacuum for 3 h.

## 2.2. NMR experiments

$^{27}\text{Al}$  and  $^1\text{H}$  NMR MAS spectra were recorded on Bruker CXP-300 NMR spectrometer (magnetic field 7.04 T, resonance frequencies 78.18 and 300.066 MHz for  $^{27}\text{Al}$  and  $^1\text{H}$  nuclei, respectively).  $^{27}\text{Al}$  NMR MAS spectra were measured in a 100 kHz frequency range, pulse width  $2\mu\text{s}$ , delay between pulses 1 s. Number of scans of free induction decay was  $10^3$ . Chemical shifts were measured with respect to aquacomplex  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  as an external reference. The samples for NMR measurements were prepared in a glove box. The samples were packed in 7 mm Andrew Beams polymethylmethacrylate rotors and were insulated from the atmosphere with paraffin. Rotation frequency was 4 kHz.

$^1\text{H}$  NMR MAS spectra were measured in a frequency range 50 kHz, pulse width  $5\mu\text{s}$ , delay between pulses 5 s. Number of scans ranged from 100 to 10. Chemical shifts were measured with respect to external TMS.

Prior to  $^1\text{H}$  NMR measurements the samples were placed in a special glass (7 mm o.d., 12 mm length) sample tubes, then insulated from atmosphere with rubber tubes equipped with a stop-cock and sealed off. Quartz rotors with rotation frequency about 3 kHz were used.

## 2.3. Testing of reactivity

The typical procedure was as follows (Table 1 entry 4): Pd/C-containing 0.38 mmol Pd, 7.4 mmol  $\text{LiAlH}_4$  and 4.0 mmol chlorobenzene in toluene were mixed in Schlenk tube under argon.

Table 1

Reduction of chlorobenzene; solvent – toluene (10 ml), C – ‘Sibunit’

No.	Reducing agent	Pd:LiAlH <sub>4</sub> :S <sup>a</sup> (mol)	Temp. (°C)	Time (h)	Conversion (%)
1	LiAlH <sub>4</sub> <sup>b</sup>	0:2:1	70	4	5
2	LiAlH <sub>4</sub> /C	0:2:1	70	4	24
3	LiAlH <sub>4</sub> /C <sup>b</sup>	0:2:1	70	4	22
4	LiAlH <sub>4</sub> -Pd/C	0.1:2:1	22	6	100

<sup>a</sup> S – chlorobenzene.

<sup>b</sup> Initial composition of solvent toluene:diethyl ether = 80:20 (10 ml).

The reaction was carried out with stirring at room temperature for 6 h.

The composition of reaction products was analyzed by gas chromatography, using a LXM-80 chromatograph equipped with a flame-ionization detector and a 2 m × 3 mm steel column with 5% 8E 30/Chromaton. Argon was used as gas carrier (60 ml/min). Most of experiments were performed at  $70^\circ\text{C}$ .

## 3. Results and discussion

The results of chlorobenzene reduction with  $\text{LiAlH}_4$ -ether solution,  $\text{LiAlH}_4$ /Sibunit and  $\text{LiAlH}_4$ -Pd/Sibunit are presented in Table 1. From Table 1 it follows that the 4 h treatment of chlorobenzene with  $\text{LiAlH}_4$  in ether/toluene (20/80%) at  $70^\circ\text{C}$  gives only 5% conversion of chlorobenzene into benzene after 4 h, but the conversion of chlorobenzene increases to 24% when using supported  $\text{LiAlH}_4$ /C.

For  $\text{LiAlH}_4$ -Pd/C-chlorobenzene system, the yield of benzene was 100% after 6 h at  $22^\circ\text{C}$ . Thus, the data of Table 1 show that reduction of chlorobenzene with  $\text{LiAlH}_4$ -Pd/Sibunit provides a high yield of benzene under mild conditions. The activation of hydrides by transition metals was reported in [3,4] where nearly stoichiometric amounts of transition metals salts were used. In our case a considerably lower amount of Pd (with molar ratio Pd:Al = 0.1:2) is sufficient for activation of supported  $\text{LiAlH}_4$ . Therefore, this sys-

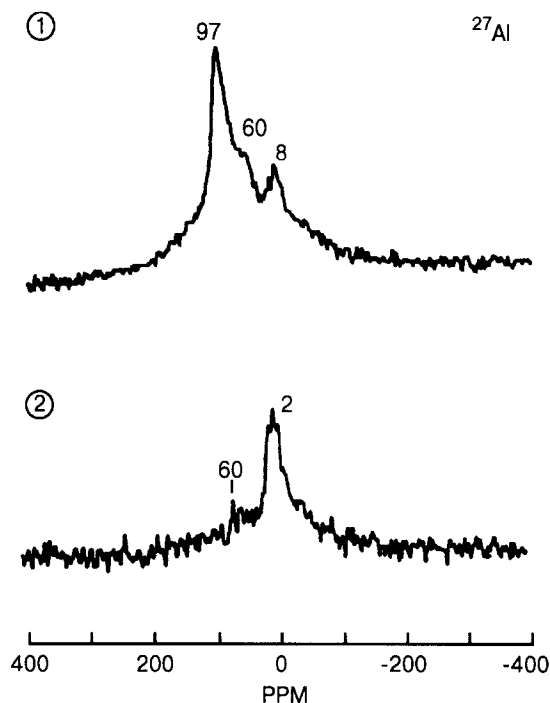


Fig. 1.  $^{27}\text{Al}$  NMR MAS spectra of catalyst 10 wt%  $\text{LiAlH}_4/\text{Sibunit}$  (1) and effect of moisture (open rotor for 1 h) upon the spectrum of the same sample (2).

tem could be useful for decontamination of chloroorganic compounds.

In order to understand the nature of the active species, we carried out the  $^1\text{H}$  and  $^{27}\text{Al}$  NMR MAS studies of supported  $\text{LiAlH}_4$  and  $\text{LiAlH}_4\text{-Pd}$  samples.

$^{27}\text{Al}$  NMR spectra of  $\text{LiAlH}_4/\text{C}$  are shown in Fig. 1. The spectrum measured immediately after sample preparation in glove box manifests the peaks at 97, 60 and 8 ppm. The peak at 97 ppm can be attributed to  $^{27}\text{Al}$  atoms in  $\text{LiAlH}_4$ , where  $^{27}\text{Al}$  is surrounded by distorted tetrahedra formed by four hydrogen atoms [9]. One can ascribe the peaks at 60 and 7 ppm to  $^{27}\text{Al}$  in tetrahedral and octahedral environment by oxygen atoms since these values are typical for  $^{27}\text{Al}$  in oxides and hydroxides [10,11]. The latter is expected to be formed by interaction with traces of oxygen and moisture during the samples preparation in a glove box. This conclusion is confirmed by experiments on hydride interaction with moisture which really show the disappearance of the signal from hydride

and increase of the peak at  $\delta=0\text{--}8$  ppm (Fig. 1, spectrum 2).

More detailed information has been obtained from  $^1\text{H}$  NMR MAS spectra, which provide the data on the state of hydrogen atoms in the samples under study.

The spectrum of 10 wt%  $\text{LiAlH}_4/\text{Sibunit}$  manifests an intensive line at  $\delta=-9$  ppm from hydride protons (spectrum 1 in Fig. 2). It appears that this value is typical for supported  $\text{LiAlH}_4$ , while a signal with  $\delta=2.8$  ppm was found for

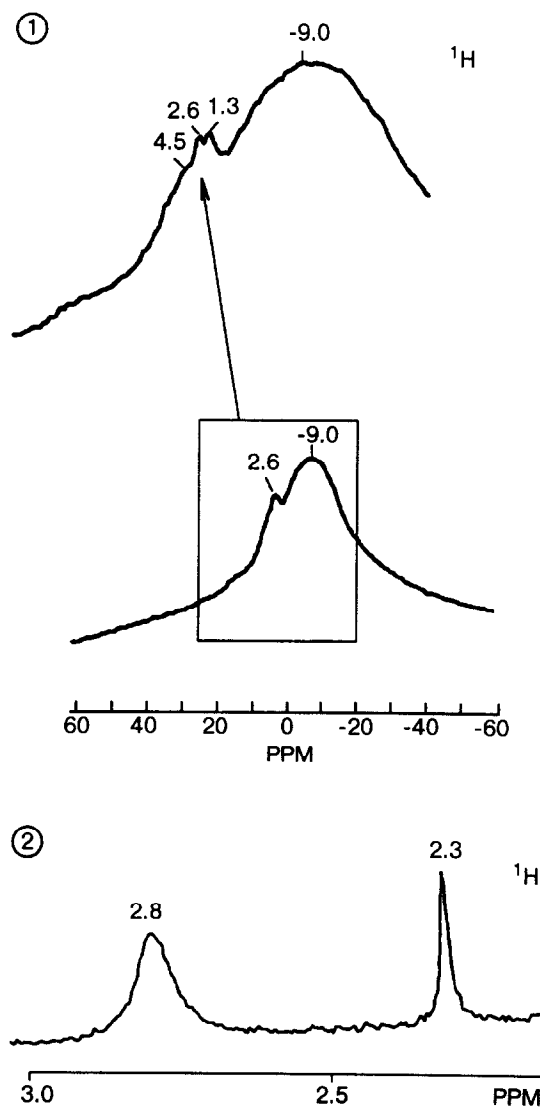


Fig. 2. (1)  $^1\text{H}$  NMR MAS spectrum of 10 wt%  $\text{LiAlH}_4$  supported on Sibunit. (2)  $^1\text{H}$  NMR spectrum of 10 wt%  $\text{LiAlH}_4$  in ether-toluene (95:5; wt.%) solution.

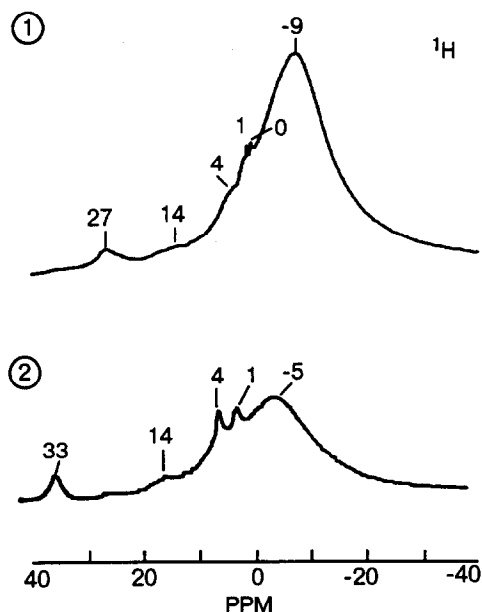


Fig. 3.  $^1\text{H}$  NMR MAS spectra of Pd-LiAlH<sub>4</sub>/Sibunit containing 10 wt% Pd and two different concentrations of LiAlH<sub>4</sub>: (1) 10 wt%, (2) 5 wt%.

LiAlH<sub>4</sub> in ether-toluene solution, where LiAlH<sub>4</sub> is coordinated by ether molecules (spectrum 2 in Fig. 2) The line at 2.3 ppm belongs to CH<sub>3</sub> group of toluene in ether-toluene solution. At the same time, in the spectrum 1 in Fig. 2 the lines of lower intensities are observed with  $\delta = 4.5$ ; 2.6 and 1.3 ppm from OH groups of carbon support which is known to have the variety of OH groups of different chemical nature [8].  $^1\text{H}$  NMR MAS spectra of LiAlH<sub>4</sub>-Pd/Sibunit system reveal the formation of new hydride species which most probably contain Pd in their structure. Fig. 3 shows the spectra at two different concentrations of LiAlH<sub>4</sub> and the same Pd concentration (10 wt%). They show that along with the line of LiAlH<sub>4</sub> hydride protons, two new lines at about 30 ppm and 14 ppm appear in the spectra. At the same time the chemical shift of hydride protons of LiAlH<sub>4</sub> changes at the decrease of its amount on reagent surface to about -5 ppm for the sample containing 5 wt% LiAlH<sub>4</sub>.

$^1\text{H}$  NMR spectra of two palladium hydrides ( $\alpha$  and  $\beta$ ) were reported [12]. These species were prepared by treatment of Pd in NaY zeolite with H<sub>2</sub> at 25°C. The signal of  $\alpha$ -hydride was observed

at low hydrogen concentrations and had a variable hydrogen composition; its  $^1\text{H}$  NMR chemical shift changed from -100 to 0 ppm with varying atomic hydrogen/Pd ratio from 0.1 to 1. Another signal with positive chemical shift (22 ppm) corresponded to the formation of  $\beta$ -hydride, which had a constant hydrogen:palladium ratio.

In this work we did not detect the formation of  $\alpha$ - or  $\beta$ -hydrides. Instead, two  $^1\text{H}$  NMR signals with positive chemical shifts indicate the formation of two new Pd hydride species. Unlike  $\beta$ -hydride the low field  $^1\text{H}$  line with chemical shift (at 27–33 ppm) dependent on Pd/LiAlH<sub>4</sub> ratio indicates the formation of new hydride species of a variable composition. A signal at 14 ppm does not change its position for two Pd/LiAlH<sub>4</sub> ratios and most probably is due to a hydride compound with fixed chemical composition. Most likely both signals correspond to the formation of hydride species which contain both Pd and  $^{27}\text{Al}$  in their structure. Participation of LiAlH<sub>4</sub> in structure of complexes seems to be supported by the change of the  $^{27}\text{Al}$  chemical shift of LiAlH<sub>4</sub> at variation of Pd/LiAlH<sub>4</sub> ratio.

#### 4. Conclusions

Thus, results presented above show that supported LiAlH<sub>4</sub> and Pd-LiAlH<sub>4</sub> are highly reactive in dechlorination of chlorobenzene, and can be considered as promising reagents for decontamination of chloro-organics. Note, that supported LiAlH<sub>4</sub> shows higher activity in hydrodechlorination reaction than LiAlH<sub>4</sub> in solution. The latter fact could be due to the negative influence of ether coordinated to AlH species in solution.

$^{27}\text{Al}$  and  $^1\text{H}$  NMR data provide important information on the types of hydride species and their interaction with support surface. Supporting of LiAlH<sub>4</sub> on Pd/Sibunit samples results in formation of two new hydride species, containing Pd and Al<sub>x</sub>H<sub>y</sub> in their structure. Taking into account the results on reduction of chlorobenzene and NMR data allows one to suggest that the formation

of the mixed Pd–LiAlH<sub>4</sub> supported hydrides may be responsible for the increase of the reactivity.

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